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(54) PRODUCTION OF SHAPED ARTICLES WITH A CELLULAR STRUCTURE

(71) I, GUNTHER WILL, a German citizen of 11 Zimmerstrasse, 61 Darmstadt, Federal Republic of Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for producing shaped articles with a cellular structure.

Cellular or porous solids may be produced by expanding curable polymerisable or plasticised masses by means of gases or vapours or by adding substances to polymerisable, liquid compounds which serve as blowing agents and which can be expelled or washed out after curing. The latter process is described in United States Reissue Patent No. 27,444. According to this process ethylenically unsaturated compounds preferably with unsaturated polyesters dissolved therein are mixed with water to form a water-in-oil emulsion which under the influence of catalysts and accelerators is cured after shaping. The water can optionally be dried out of the finished product.

According to the process of German DOS No. 2,046,575, certain non-ionic emulsifying agents may be used which consist of a polyalkylene oxide block copolymer with a hydrophobic portion. According to this process by adding these emulsifying agents thermosetting resins are processed which are initially pre-cured and then finally cured at temperatures from 50° C to 100° C and above. Similar emulsifying agents which consist of hydrophobic polymerisation products of organic compounds containing —CH_2—CH_2—O— groups as hydrophilic components are described in German DOS No. 1,455,227. By curing the polymerisable portion of the emulsion at elevated temperatures a not inconsiderable proportion of the emulsified water is expelled from the polymer.

German DOS No. 1,928,026 describes a variation on this process which substantially leads to the formation of open cells. According to this modified process wetting agents and pulverulent solid polymers are also added in specific mixing ratios to the polymerisable portion of the emulsion which in addition to the liquid polymerisable phase contains water and water-in-oil emulsifying agents. After polymerisation of the water-in-oil emulsion the water is removed. Products with a coarse cellular structure having a limited flow resistance for liquids and gases and very good material characteristics are formed from the polymer.

In addition Belgian Patent No. 785,091 describes a process according to which open-cell moulded articles which can be easily dehydrated are obtained from solid bodies which contain as the water-in-oil emulsion unsaturated polyesters, unsaturated copolymerisable monomers together with other components such as emulsifying agents which as regards their molecular structure are based on already known emulsifying agents.

As compared with other cellular products which, immediately after foaming or a short time thereafter, have an adequate stability of shape, the products obtained according to the above indicated processes have the disadvan-

tage that they subsequently undergo considerable shrinkage which can vary even when the same production conditions are maintained. In addition the cellular structure of the products obtained according to these known processes which, for the same pore volume can vary considerably, can only be influenced to a very limited extent by special reaction conditions.

The object of the present invention is to provide a new process for the production of shaped articles having a cellular structure with a high proportion of open cells.

Thus according to the present invention there is thus provided a process for producing shaped articles with a cellular structure which comprises shaping and curing an emulsion comprising from 25 to 90 parts by weight of water dispersed in from 75 to 10 parts by weight of a liquid synthetic resin-monomer mixture comprising styrene and/or a methacrylic or acrylic acid ester and a copolymerisable unsaturated polyester or copolymer of styrene and butadiene, the emulsion having a dispersion level which is in the characteristic range (as herein defined) prior to commencement of curing and the curing being effected at a rate whereby the emulsion gels before commencement of disintegration of the emulsion.

The emulsion may if desired additionally contain one or more further ingredients selected from curing catalysts, emulsifying agents, wetting agents, accelerators, inhibitors, cross-linking compounds, softeners, fillers and dyes.

The expression "characteristic range" is used herein to define a dispersion level range extending from a lower limit at which the water-in-oil emulsion can be cured to a shaped article whose volume amounts to at least 90% of the volume occupied by the emulsion prior to commencement of curing to an upper limit at which the water-in-oil emulsion can be cured whilst maintaining at least 90% of the emulsion volume prior to commencement of curing to a shaped article with a continuous fine-porous structure which loses at least 20% of the weight of the water contained in the cured emulsion from a sample with a ratio of surface to volume of 1.17:1 when dried at a temperature of 23° C and a relative humidity of 60% for 24 hours.

The characteristic range as defined above extends from a dispersion level at which dispersion has just commenced and is minimal up to a level at which there is an onset of stable dispersion formation i.e. formation of an emulsion which will not change its phase structure upon subsequent curing and which does not decompose as a result of phase change.

The characteristic range of the dispersion level following the increasing dispersion of the dispersed phase can be regarded as being capable of subdivision into a lower, medium and upper portion. If the dispersion level of the emulsion is set to a value which is in the lower portion of the characteristic range, by curing of this emulsion shaped articles are obtained whose base or outer surfaces have distributed over them a closed and non-porous polymerisation layer whilst the remaining portions of the shaped article form a coarse to fine cellular structure. These shaped articles have a sandwich character, whereby the thickness of the closed layer and the cell diameter of the cellular layer decrease with increasing dispersion level of the emulsion. Inasfar as the cells of the cellular layer are open-celled the water, optionally after opening the closed dense polymerisation layer, can be removed by suction or dried out. If the dispersion level of the emulsion is set to a value which lies in the middle portion of the characteristic range shaped articles are obtained having a medium to fine structured core surrounded completely by a thin dense polymer layer. Within this portion of the characteristic range the skin-like layer becomes thinner and finally permeable with increasing dispersion level of the emulsion. In the same way with increasing dispersion level of the emulsion the cellular structure of the core becomes finer. From these shaped articles the water contained in the cells of the core can be removed despite the presence of the closed, thin, outer layer by suction by opening this layer or can be expelled by drying, provided that the cells of the core are open. On setting the dispersion level to a value which lies in the upper portion of the characteristic range shaped articles are obtained whose surface has no resin deposits and which overall consists of a very uniform fine cellular structure with open and/or closed cells. With increasing dispersion level of the dispersion phase in the emulsion the diameter of the cells of the shaped articles produced from the particular emulsion becomes increasingly smaller. On further increasing the dispersion level the emulsion passes into the state of absolute stability and in this state can be completely cured. The onset of this dispersion state occurs at the upper extremity of the characteristic range as herein defined. Inasfar as the emulsion is present in the state of absolute stability its curing leads to shaped articles which either do not give off the water or only give it off with difficulty.

The state of absolute stability of a true water-in-oil emulsion was hitherto the declared objective in the production of porous solids from water-in-oil emulsion in order to eliminate as far as possible the necessity of expelling the water. However, disadvantages were encountered, namely the often considerable shrinkage occurring with the prolonged drying and the increased weight resulting from the quantities of water remaining therein.

The monomer content of the synthetic

resin-monomer mixture used in the process according to the invention comprises styrene and/or an ester of methacrylic or acrylic acid such as for example methyl methacrylate, ethyl methacrylate, glycol methacrylate, 1,4-but-2-ene dimethacrylate, cyclohexyl methacrylate, ethyl acrylate or 1,2-propanediol diacrylate. The mixture may also if desired contain additional monomers, e.g. a nitrile such as for example acrylonitrile.

The monomer component of the mixture can if necessary serve as the solvent or diluent for the synthetic resin portion. This resin portion can be a high molecular weight unsaturated polyesters or a copolymer of styrene and butadiene which is copolymerisable with the monomer or monomer mixtures. Particularly suitable are unsaturated polyesters which are obtained by condensation of dihydric alcohols, such as for example ethanediol, 1,2-propandiol, 1,3-propandiol, diethylene glycol, 1-allyl-2,3-hydroxypropandiol, and unsaturated $\alpha\beta$-ethylenically unsaturated dicarboxylic acids, such as for example maleic acid, fumaric acid and the like. In addition the unsaturated polyesters can also contain di- and polyvalent carboxylic acids, such as for example endomethylene tetrahydrophthalic acid, tetrahydrophthalic acid, phthalic acid, succinic acid, adipic acid, propionic acid, benzene tricarboxylic acid and benzene tetracarboxylic acid, and also other low grade alcohols such as benzyl alcohol, 1,2-di-(allyloxy)-3-propanol-glycerol, pentraerythritol, as well as hydroxy-carboxylic acids, such as e.g. 4-hydroxy-methylcyclohexane carboxylic acid. The use of these substances for expanded resin products is described in United States Reissue Patent No. 27,444, German DOS No. 2,046,575 and German DAS Nos. 1,024,654, 1,067,210 and 1,081,222. In conjunction with self-emulsifying polyesters it is also possible to use epoxide compounds with more than one epoxide bond as the polymerisable phase, as indicated in German DOS No. 1,495,843.

It is particularly advantageous to use a mixture of styrene and methyl methacrylate in the weight ratio 1:4 to 4:1 as monomer together with an unsaturated polyester copolymerisable therewith. In addition it is also possible to add to the emulsion polymers of high molecular weight which do not copolymerise with the monomer. These are preferably polymers of styrene, vinyl chloride, esters of methacrylic acid and optionally unsaturated polyesters which are copolymerised with monomers such as e.g. styrene, methyl methacrylate etc.

In order to emulsify an emulsion of the water-in-oil type, an emulsifying agent is generally used whose molecules consist of hydrophobic and hydrophilic portions. Such emulsifying agents may be used individually or in admixture.

Emulsifying agents which partially separate in the monomer portion of the water-in-oil emulsion in the presence of water have proved to be particularly suitable. The suitability of such emulsifying agents can be proved by a simple test. For this purpose, 5 to 10% by weight of the emulsifying agent or mixture of emulsifying agents to be tested are dissolved in the monomers of the synthetic resin-monomer mixture to be used in the process. A few drops of water are added to about 10 cc of this solution. In the case of particularly effective emulsifying agents the introduction of the water leads to a visible separation.

Examples of low molecular weight water-in-oil emulsifying agents are esters of higher fatty acids with polyhydric alcohols, amides of higher fatty acids and salts of alkylsulphonic acids. From the very large number of high molecular weight compounds, particularly suitable are polymers or polycondensates which are completely or almost completely water-insoluble and which containing hydrophilic groups such as for example carboxyl, carboxylate, carboxamide and hydroxyl groups, ester or ether groupings, amino, ammonium, sulphonic acid and/or sulphoxide groups. Such emulsifying agents are for example described in German Patent 1,301,511. Copolymers with an acid number between 8 and 12 which consist of a polymerisable carboxylic acid such as acrylic acid for example on the one hand and styrene on the other, and wherein the free carboxyl groups are wholly or partially neutral with organic or inorganic bases can be used with equal success. It is also possible to use polymers or copolymers of styrene, methyl methacrylate or vinyl acetate as the emulsifying agent if these polymers or copolymers are produced in emulsion polymerisation processes in the presence of persulphates and consequently contain sulphonic acid groups. Saturated and unsaturated polyesters can also be effective as emulsifying agents, particularly if they are partly or completely saponified with alkalis or if they contain an adequate number of free carboxyl groups. These emulsifying agents are for example described in detail in German DAS No. 1,199,982 or German Patent specification 1,267,845. These can be the same polyesters as are also used as the resin component of the resin-monomer mixture. It is also possible to use graft copolymers which are produced in the presence of polyalkylene oxides from styrene and which are described for example in German DAS No. 1,169,671 as emulsifying agents. It is also possible to use film-forming polymers such as e.g. cyclised rubber or copolymers of vinyl compounds with a group having 8 C-atoms described in German DAS No. 1,148,382 as emulsifying agents. It is also possible to use as emulsifying agents hydrophobic polymerisation products of organic compounds which contain 0.5 to 60%, preferably 28 to 55%

by weight of oxyethylene groups as hydrophilic components. Preferably the hydrophobic portion of these emulsifying agents can be composed of polyoxypropylene and must then have a molecular weight of over 600. Also copolymers with a total molecular weight of above 800 which contain 90 to 20% by weight of polyoxypropylene glycol and 10 to 80% by weight of polyoxyethylene glycol are suitable emulsifying agents such as are known from German DOS No. 1,495,227. Further suitable emulsifiers are described in German DOS Nos. 2,046,575 and 1,928,026. The effectiveness of the emulsifying agents soluble in the organic phase can be increased by water-soluble low molecular weight organic compounds which contain both a hydrophilic and a hydrophobic proportion. Compounds of this type are in particular alcohols, organic acids, ethers, ketones, wetting agents and the like. It is understood that the above-indicated emulsifying agents can be used individually or in mixture. The quantity of the emulsifying agent or mixture of emulsifying agents to be used is set according to the desired dispersion level of the emulsion and is preferably in a range from 0.05 to 10% by weight. 25 to 90 parts by weight of water are then emulsified in 75 to 10 parts by weight of this polymerisable mixture. In order to disperse the water in the organic phase conventional stirrers, dissolvers or similar apparatus can be used.

In order to cure the emulsion, curing catalysts and accelerators are conveniently added. The curing catalysts can be water soluble such as e.g. alkali, formaldehyde, sulphoxylates, persulphates, hydrogen peroxide, sodium hydrogen sulphite and cobalt chloride. However, it is also possible to use catalysts or accelerators such as benzoyl peroxide, lauroyl peroxide, ethyl methyl ketone peroxide, cyclohexanone peroxide, azodiisobutyryl nitrile, N,N-diisopropyl-p-toluidine, tertiary amines, such as dimethylparatoluidine, dimethyl- or diethylaniline and cobalt naphthenate, which are soluble in the polymerisable phase. In some cases it can be advantageous to use in addition to a water soluble catalyst or accelerator one which is soluble in the polymerising phase. These catalytically active substances are with advantage added in quantities of 0.1 to 10% based on the total weight of the emulsion. Furthermore inhibitors (such as e.g. 4-ethyl-pyrocatechol, 3-methyl-pyrocatechol, tertiary butyl pyrocatechol, toluquinol, quinol, 2,5-di-tert . - butylquinone, p - benzoquinone), cross-linking compounds, softeners, fillers and dyes may be added as desired to the emulsion prior to curing.

During the emulsification of the water in the polymerisable phase the emulsion is initially set to a dispersion level in the characteristic range for the particular emulsion.

The dispersion level of the emulsions with the same composition can be measured by physical characteristics such as e.g. the electrical conductivity, light permeability or viscosity of the emulsion.

Hereinafter the invention is described using the viscosity as a measure for the dispersion level. If from water and a particular resin-monomer mixture different emulsions of the water-in-oil type with increasing viscosity are prepared, then at constant temperature it is observed that the stability of the emulsion is dependent on its viscosity. All percentages referred to hereinafter are by weight unless otherwise specifically stated.

Fig. 1 shows the disintegration time in minutes of an emulsion of 50% by weight water at 20° C in a mixture of 52 parts by weight of unsaturated polyesters, 20 parts by weight of methyl methacrylate and 28 parts by weight of styrene with an increasing emulsifying agent content of 0.1, 0.2, 0.6 and 3.0% by weight, as a function of the viscosity in cP. The polyester has an acid number of 34 and is modified with 35% by weight of styrene and has a viscosity of 1200 cP. The emulsifying agent used comprises a mixture of etherified alcohols in a weight ratio of 1:1 containing as one component an emulsifying agent Pluronic 105 ("Pluronic" is a registered Trade Mark) and as the other component the emulsifying agent Pluronic 127. For the emulsification of the water in the polymerisable phase the mixture was stirred for 2.5 minutes using a normal flat paddle mixer with 800 to 1000 r.p.m. The rise in viscosity was brought about by the addition of increasing quantities of emulsifying agent. The disintegration time in minutes was measured as the time starting at the end of the stirring time up to the first signs of emulsion separation by phase division in the centre of the emulsion column or of settling of the water. As is shown by the figure the first signs of disintegration appear at an emulsion viscosity of 600 cP after 45 minutes and at a viscosity of 3800 cP after 700 minutes.

Fig. 2 shows the percentage water loss as a function of the viscosity of the emulsion which a sample of the cured emulsion undergoes in a particular time under specific conditions. The values of the curve shown in Fig. 2 were measured on an emulsion produced in accordance with the above details. To increase the dispersion characteristics of the water 0.1 to 2% by weight of emulsifying agent (based on the polymerisable portion of the emulsion) were added to this emulsion in increasing quantities. Three samples were produced from an emulsion with a particular emulsifying agent content and which had been stirred for 1, 2 and 5 minutes using a flat paddle mixer at 800 to 1000 r.p.m. The emulsion temperature was kept at 25° C, whereby the gelling time was set at 10 minutes. At the end of stirring the viscosity was measured with a rotary viscosimeter with a

spindle at 300 to 10,000 cP. In each case 170g of such a sample emulsion was poured into a square moulding dish with an area of 7.75 × 7.75 cm and cured. The thickness of the sample was 2.75 cm. After removing from the mould the weight of the sample was determined and consequently also the water separation which occurred during curing. Subsequently the sample was suction filtered with a water jet pump at about 20 Torr for 3 minutes whereby the suction surface represented about 10% of the complete surface area. The weight of the sample was again determined. The samples were stored under normal conditions in a closed space for 4 days and then weighed again. The result of these tests are given in Table 1.

TABLE 1

Emulsifying agent content (in % by wt. of polymerisable portion of emulsion)		Stirring time in min. at 800 to 1000 r.p.m. 1'	2.5'	5'
0.1	Viscosity in cP	380	520	600
	Weight in g after curing	164	165	164
	Weight in g after suction filtering	162	152	115
0.5	Viscosity in cP	1400	2100	2400
	Weight in g after curing	165	167	169
	Weight in g after suction filtering	119	131	147
1.0	Viscosity in cP	1700	2600	3300
	Weight in g after curing	165	167	168
	Weight in g after suction filtering	119	139	150
2.0	Viscosity in cP	2500	3700	4200
	Weight in g after curing	168	168	167
	Weight in g after suction filtering	135	151	159

If the thus determined water contents are arranged according to increase in viscosity, which varies according to the emulsifying agent content and stirring time, then the following values are obtained:

TABLE 2

Viscosity cP	Weight in g after curing	Weight in g after suction filtering	Water loss %	Weight in g 4th day	Residual water %
380	164	162	9.4	130	52.9
520	165	152	15.3	110	29.4
600	164	115	64.7	85	—
1400	165	119	60.0	87	2.3
1700	165	119	60.0	88	3.5
2100	167	131	45.8	88	3.5
2400	169	142	32.9	90	5.8
2500	168	135	41.2	93	9.4
2600	167	139	36.4	90	5.8
3300	168	150	23.0	90	5.8
3700	168	151	22.0	97	14.1
4200	167	159	12.9	100	17.6

It can be seen from Fig. 2 that the water loss of the samples varies with the emulsion viscosity although the viscosity of the emulsion is obtained by varying the emulsifying agent content and by changing the stirring time. After a rapid rise in water loss with increasing viscosity of the emulsion, at 1000 cP the water loss then declines with increasing viscosity of the emulsion. With an emulsion viscosity of 4000 cP the water loss is only about 10% which represents the quantity of water separated off during curing of the emulsion. The same trends are observed in the quantities of water extracted from the samples by drying at a temperature of 23° C at a relative humidity of 60% for four days. Here again the quantities of water given off initially increase with the emulsion viscosity and then after reaching a maximum decline again with higher viscosity values of the emulsion. It is therefore possible to observe a relationship between the viscosity or dispersion level of the emulsion and the speed with which water is given off by the moulded articles obtained by the curing processes.

However, the cellular structure of the samples obtained also shows an inter-relationship with the viscosity of the emulsion from which these samples are prepared. In a viscosity range up to about 300 cP the resin-monomer mixture is deposited on the base of the mould whereby the coating thickness of the separated resin decreases with increasing viscosity; thus the thickness of this deposited coating can be determined by setting the viscosity. Above this dense and non-porous coating is arranged a cellular structure with cells of approximately 100 to 5000 μ diameter. In the viscosity range 300 to 600 cP the deposited coating of the polymerisable phase is reduced again and a thin, but dense coating is formed around the complete moulded article. The core of the moulded article comprises a medium to fine celled open cellular structure wherein the cells have a diameter of approximately 50 to 1000 μ. The water can only be removed by suction from these moulded articles if the dense resin coating is pierced at the suction point. In the viscosity range between 600 and 1500 cP the dense outer skin becomes increasingly permeable and thin so that the quantity of water which can be removed by suction very rapidly rises. The core of this cellular body comprises an open cellular structure with cells with an approximate diameter of 50 to 500 μ. The density of the outer skin further declines in the case of moulded articles produced from an emulsion with a viscosity of 1500 to 2500 cP. The water can be very readily removed by suction from these moulded articles and the core thereof comprises a cellular structure having cells with a diameter of approximately 10 to 100 μ. Moulded articles produced from emulsions with a viscosity of 2500 to about 3500 cP no longer have an outer skin but nevertheless only a small amount of water can be removed by suction from these moulded articles. Surprisingly from these moulded articles however the water can be expelled at moderate temperatures between 20 and 40° C at a high speed. Furthermore the moulded article has an extremely fine cellular structure. In the case of moulded articles produced from an emulsion with a viscosity of 3000 to 4000 cP the amount of water which can be removed by suction drops to zero. Only during the curing does the moulded article lose a little water. This phenomenon was observed on all the moulded articles. The drying rate of these moulded article is also less than the above-described moulded articles. During the curing of an emulsion whose viscosity is higher than 4000 cP no more water can be removed by suction from the moulded articles produced therefrom and even the drying of the moulded article only brings about a water loss of a maximum of 10% by weight. The described changes occur continuously. The hereinbefore described terminal state of an absolutely stable emulsion can also run into a disintegration of the emulsion and phase change.

About 48 hours after curing, the sample which has just been described reveals on a smooth freshly cut surface a fine light coloured dry coating running parallel to the outer surface of the sample, which is clearly distinguished from the darker moist core. The other samples from the above-indicated tests reveal in cross-section a wide white dry layer which only in certain cases gradually passes into a moist residual core. They are capillary-active and absorb liquids.

These inter-relationships between the dehydratability and the structural form of the sample on the one hand and the viscosity or dispersion level of the emulsion on the other apply for any emulsion system which is obtained by emulsifying water in a polymerisable or hardenable phase consisting of a resin-monomer mixture. However the dispersion level of the emulsion is considerably influenced by the numerous components present and active in the emulsion so that each emulsion system has a characteristic dispersion level range within which the process according to the invention must be performed. This characteristic dispersion level range can be determined by simple tests for each emulsion system by measuring the emulsion viscosity. The end of the characteristic dispersion level range of an emulsion system is reached at the viscosity of the particular emulsion at which a sample produced from this emulsion and cured after drying at a temperature of 23° C and a relative humidity of 60% for 24 hours, has a water loss of 20% or less. In Fig. 2

a water loss of 20% of the sample corresponds to the viscosity of the emulsion of 3250 cP.

If the dispersion of the water in the resin-monomer mixture is still further increased and consequently the viscosity of the emulsion is further increased, then by curing of the resin-monomer mixture, completely impermeable porous moulded articles are obtained from which no water can be removed by suction and which even on drying at a temperature of 23° C and a relative humidity of 60% only very slowly give off the water.

Therefore the viscosity of an emulsion from which a standard moulded article with a ratio of surface to volume of 1.17:1 can be cured and which after drying at 23° C and a relative humidity of 60% for 24 hours loses 20% or less of the water contained in the moulded article or which correspondingly after this time still contains 80% or more of its original water content marks the end of the dispersion phase at which there is still an opening of the phases of the emulsion.

The emulsion can however pass from the state of phase opening into the state of phase change particularly if the water content of the emulsion is well above 50%.

The characteristic range of the dispersion level and the viscosities corresponding thereto can obviously vary considerably from one emulsion to another. The numerous components such as emulsifying agents, resin types, catalysts, etc., influence the characteristic range of the dispersion level as do the relative proportions of the individual components.

According to the invention it is also necessary to cure the emulsion at a rate whereby the emulsion gels before commencement of disintegration of the emulsion. The relevant gelling time (F) of the emulsion is related to the viscosity in the following manner:

$$\frac{\text{Viscosity in cP}}{\text{Gelling time in min.} \times 100} = F$$

The value of F, which can be determined once and for all and in simple manner by means of a test series can be plotted in a graph as a function of the viscosity, from which it is possible to simply read off the gelling time necessary for producing a particular product.

By means of the process of the invention it is now possible by adjusting the dispersion level of the emulsion to determine, within a characteristic range for each emulsion composition, the type and pore size of the polymer obtained by curing this emulsion. This dispersion level can be determined by measuring and monitoring guidance parameters such as e.g. viscosity, conductivity, turbidity of the emulsion or similar physical parameters. Hitherto in this field every effort was made to use highly stable emulsions with a high dispersion level, in order to obtain ultra-fine cellular products therefrom in short gelling times, which did not take into account the stability behaviour of the emulsion under the influence of the curing process. However then products were obtained from which the water could only be removed by heating or as a result of long drying times. In contrast, according to the process of the present invention, whereby the product type is determined from the characteristics of the emulsion, products are obtained from which at least 20% of the water contained therein can be removed within a period of 24 hours at 23° C and a relative humidity of 60%.

Whereas hitherto every effort has been made to increase the dispersion level of the emulsion to such an extent that the emulsion even after prolonged standing reveals no disintegration phenomena and is therefore completely stable, in the process of the invention the curing of the emulsion is performed at such a dispersion level that during curing there is phase opening of the emulsion and it is therefore unstable. Only through this special measure of the inventive process is it possible to obtain a plurality of differently composed end products.

It has also been found that the shrinkage of water-containing cured products is substantially dependent on the drying time, whereby shrinkage increases in almost the same proportion as the percentage water loss rises as shown in Fig. 3. By checking the weight loss and the decrease in length of a few hundred material samples, produced using polyester cast resins containing ingredients of all kinds and cast in the form of rods (26 × 34 × 580 mm), for up to 150 days it was possible to establish the shrinkage pattern and its dependence on the water content. It was thereby proved that rapid dehydration of moulded articles produced from water-in-oil emulsions of polymerisable compounds is necessary if stability of shape is desired.

In Fig. 3, WVI represents water loss as a percentage and SZII linear shrinkage as a percentage.

According to the process of the invention the water-in-oil emulsion is with particular advantage set to the dispersion level which after 24 hours is in the range of optimum water loss. This ensures as with other cellular plastics that dimensional stability is achieved even after 2 to 6 days.

By means of the new process not only is the reproductibility of the material characteristics safe-guarded and the range of utilisation considerably increased by the diversity of the material structure but technical advantages are also obtained which permit a considerable simplification of processing.

Since the viscosity of the emulsions is adjusted via the quantity of emulsifying agent used and the stirring intensity, and since these

factors may be varied widely although not in a completely unlimited fashion as can be shown from the tests series in Table 2, a considerable technical advantage can be obtained in that from a hardenable water-in-oil emulsion, by adjusting the viscosity via a stirrer the structural characteristics of the cured products can be controlled, by means of the water quantity the density may be controlled, and by means of the emulsion temperature the curing pattern may be controlled, whilst all the other components remain constant. These advantages are in particular available during the continuous production of a water-in-oil emulsion, and in addition it is possible to adjust the production quantity per hour by regulating the quantities of water and resin which pass through the mixer.

Obviously constants can be replaced by other variants e.g. the viscosity can be regulated exclusively via the quantity of the emulsifying agent supplied with constant stirring intensity. It is also however possible to control simultaneously the quantity supply of several components of the emulsifying agent system and thereby regulate dispersion. This means that with e.g. an unsaturated polyester resin already containing emulsifying agents, accelerators, inhibitors and a corresponding quantity of monomers, the characteristic dispersion range can be determined and merely by taking account of the water quantity temperature and viscosity setting the dispersion level can be given with which particular structural conditions in the end product are achieved.

The process of the invention permits the production of in particular open-pored products which, especially if the water content is above 50% by weight permit the removal of the water in a very short time. In particular, it is in the range which was hitherto considered uninteresting due to the difficulties of water removal that it has proved possible to produce new materials of very fine porosity. 4 cm thick plates with a water content between 50 and 60% by weight and above can be dehydrated by up to 87% in a few minutes. The remaining water content is dried out under normal room temperatures of 23° C and circulating air within 24 to 50 hours. Thus the necessary dimensional stability is obtained within 3 days. The additional provision of the moulded articles with a solid and dense resin outer layer opens up completely new possibilities of use. The emulsions can be sprayed with glass fibres without difficulty so that sandwich-like moulded articles with a high strength having an outer layer of glass fibre reinforced material and an inner portion of emulsion with a high water content may be produced therefrom.

The fields of utilisation indicated in numerous publications and patent specifications can be exploited in the same way by the process of the invention. The products of the invention may thus be used for example as decorative advertising materials, containers, frames, light coverings, musical instruments, furniture and furniture fittings, equipment for shops and counters, devices, casings, structural members, partitions, doors, door frames, wall coverings in the form of plates or as a sprayable coating with and without fillers, replaceable casings and forms in concrete construction, road markings, road coverings, insulating materials in ship and boat construction, toys, model masses which can easily be machined, do-it-yourself materials for schools and model construction in place of wood, artificial leather which can breathe, etc.

The curing can in particular take place in thin layers by the action of ultra-violet light or hard rays.

The very rapid dehydration particularly at atmospheric pressure or under vacuum and the drying which can be completed in a few hours at temperatures between 15 and 25° C or at higher temperatures up to about 150° C which has now been achieved make it possible for even thick members with wall thicknesses of several centimeters (5 cm and more), particularly large members (semi-finished products such as plates and sections), to be produced continuously. Pipes can be produced by centrifuging and small portions by centrifugal casting, whereby the resin separation at the surface can be brought about in the desired directions and parts of the surface.

Through the selection of the monomeric starting materials the material structure can also be controlled. As can be seen from the tests already described, combinations of styrene and methyl methacrylates with unsaturated polyesters are particularly advantageous. It has been found that mixtures of styrene and methyl methacrylate of 1:4 to 4:1 by weight provide products which can be dehydrated particularly rapidly. The emulsions can be processed in mono and multi-component processes, whereby one emulsion portion contains the catalyst and the other the accelerator.

The emulsions can be applied by coating, casting, spraying with or without fillers, e.g. glass fibres and finally by moulding, whereby in particular moulding with fillers and fibres of any type is of great interest. As a result of the various processing variants it is possible to fully utilise the advantages offered by the process according to the invention. Consequently, by moulding and spraying products with optimum dehydrating characteristics etc., can be obtained. The subsequent viscosity change which can be caused by the spraying process must be duly considered and taken into consideration when setting the dispersion level.

The above-indicated series of tests has already provided an explanation of the fundamental procedure according to the invention. The following tests supplement this in an

exemplified manner and show the technical advantages obtained through use.

In the following tests in variant (A) the water-in-oil emulsion is prepared by initially mixing the polymerisable or hardenable constituents with emulsifiers and accelerators and then stirring into this mixture water and catalysts thus forming a water-in-oil emulsion whereby the temperature of the emulsion is adjusted with the temperature of the water. The emulsion is shaped and cured in accordance with the process of the invention. According to variant (B), one proceeds as in (A) but one water-in-oil emulsion is mixed only with accelerators and the other water-in-oil emulsion only with catalysts. Both emulsions are mixed prior to shaping and curing.

Acording to variant (C) an emulsion is prepared as in (A). However, no addition of accelerator takes place. The emulsion is brought to a temperature of 90° C after shaping and is then cured. To determine the dispersion level and dispersion range in each case 3 to 5 samples were prepared whereby the quantity of each sample represents 200 cc of emulsion. After checking the emulsion relative to its viscosity 170 cc of the emulsion are poured into a polyethylene mould with base dimensions 75 × 75 mm. After curing the sample and removing from the mould the following were determined:

1. The initial weight;
2. The sample was suction filtered for 3 minutes with a suction surface representing 10% of the total surface area and at a pressure between 14 and 20 Torr;
3. The sample was then exposed to drying at 23° C in circulating air conditions for 24 hours and the weight was determined after 24 hours;
4. After normal drying at 23° C without circulation the weight was again checked 4 days after production.

The 3 to 5 samples obtained reveal a dispersion spectrum as shown in Figs. 4 and 5 in the viscosity curves. Simultaneously the residual water values determined show the material structures changes corresponding to the viscosity pattern.

Hereinafter with various starting materials and emulsifying agents the relevant dispersion ranges are determined and in the following tests with the aid of the indicated dispersion ranges a particular dispersion level is set which leads to a pre-determined structural change of the cured samples.

The following tests show in exemplified form that by setting the dispersion level drastic changes in the cured samples result as regards their material structure which in particular effects the excellent dehydration and other properties as described hereinbefore. In all the tests of Tables 4—6 (hereinafter also referred to as Examples 4 to 6), the emulsions used were curable to shaped articles whose volume amounted to at least 90% of the volume occupied by the emulsion prior to the commencement of curing and were thus at a dispersion level above the lower limit of the characteristic range as herein defined. The tests when the weight loss after 24 hours expressed as a percentage of the total weight either with or without suction filtration is given as at least 20% by weight were carried out with emulsions having a dispersion level below the upper limit of the characteristic range as herein defined and thus these tests are illustrative of the process according to the invention. The remaining tests where the weight loss after 24 hours expressed as a percentage of the total weight either with or without suction filtration is less than 20% by weight were carried out with emulsions having a dispersion level above the upper limit of the characteristic range as herein defined; these tests do not illustrate processes according to the invention and are present for purposes of comparison only. In this regard, it should be explained that the suction filtration carried out in some tests does not in general significantly affect the performance of samples in the drying test.

In the examples of Table 4 the tests 1 to 12 (hereinafter referred to as examples 4/1—12) are performed in accordance with variant A.

In examples 4/1—6, the emulsifying agent used is a copolymer of styrene and acrylic acid with an acid number of 8—12 and in examples 4/4—6 in addition a wetting agent is used. In examples 4/1—3 and 4/4—6 it is shown that there is clearly an optimum dehydration in a specific range i.e. as in example 4/1 and example 4/4.

Example 4/1 shows on the surface after curing a completely smooth scratch-proof layer which is obtained by resin separation. Example 4/3 is a completely fine porous polymer. Examples 4/4 and 4/5 reveal a resin separation on the surface whilst example 4/6 is a completely fine porous product.

In examples 4/7—9 the emulsifier used is a block polymer of polypropylene and polyethylene oxide (Pluronic 122 and 103).

Example 4/7 provides a product which is covered with a hard glassy layer whilst the inner portion has a porous structure. A considerable proportion of water can be removed by suction filtering after opening the outer layer. In examples 4/8—9 the surface layer obtained by resin separation is greatly reduced and the surfaces are scratch proof. In example 4/9 the water can be removed by suction through the thin resin surface layer.

Examples 4/10—12 show the maximum dehydration with a water content of the emulsion of 66, 70 and 75% by weight using

Pluronic types which are here particularly well suited as emulsifying agents. After only 24 hours, even without suction filtering of the water, drying at 23° C causes more than 90% of the water introduced to be given off. The hitherto known optimum value was about 30%.

The examples of Tests 1—14 of Table 5 (hereinafter referred to as examples 5/1—14) are also performed according to variant A. However, in examples 5/1—14 the accelerator used is cobalt octoate, the catalyst methyl ethyl ketone peroxide and the promoter dimethylaniline. As this accelerating system leads to very short curing times an inhibitor is added in small quantities. Those resins are used which can be cured with this accelerating system.

Examples 5/1 and 5/2 show that an adequate emulsification is obtained by adding only large quantities of a cobalt salt, whereby however after curing products are obtained which only give off the water during the polymerisation process in very limited quantities. Examples 5/3 to 5/5 show the concomitant use of Pluronic 108 in accordance with German DOS No. 2,045,575. According to this process the emulsifying agent used leads to products which can be dehydrated particularly rapidly. The three examples show that as compared with tests 5/1 and 5/2 without an emulsifying agent only slightly improved dehydration is obtained with cold curing.

Examples 5/6—11 relate to tests with other Pluronic emulsifying agents (105, 123) whereby it is clearly visible that an optimum dehydration is obtained in a narrowly limited range of dispersion level setting (Examples 5/6 and 5/9) and they show that the dehydration can be increased more than 10 times under the same conditions by adjusting the dispersion level (Example 5/6 and 5/9). After 96 hours as compared with example 5/1 to 5/5 there is a 20 to 30 times rise in the water loss.

Examples 5/12—14 show the use of an emulsifying agent according to Belgian patent 785,091 (Example A). Here again with selected dispersion levels this emulsifying agent reaches an optimum in example 5/12. It can also be seen that by adding larger quantities of emulsifying agent the drying after 24 hours is accelerated (Example 5/14) but over a period of 96 hours the dehydration rate considerably decreases because the products are strongly hydrophilised by the increase in addition of emulsifying agent and the drying is increasingly slowed down. In Table 6, examples 6/1—3 (i.e. Tests 1—3 of Table 6) once again use Pluronics as emulsifying agents. In the optimum range after only 24 hours a dehydration of 82.3% is obtained.

Examples 6/4—7 show products with the concomitant use of soft polyester cast resin types which can be used in the same way. Here the emulsions according to variant B are used. In each case one emulsion with a catalyst and another emulsion with an accelerator are prepared and are mixed prior to use. The viscosity is determined after mixing the two components. In these examples once again when using the emulsifying agents already employed in the optimum dispersion level there is a dehydration with a water loss after 24 hours between 72.9 and 91%.

In Examples 6/4—7 the sample according to example 6/5 shows a clear resin separation on the surface whereas the samples according to examples 6/6 and 6/7 have a fine porous structure throughout.

Examples 6/8 and 6/9 demonstrate the process using soft polyester cast resins and acrylates. The performance of the examples takes place according to variant A. A leather-like product is obtained which in example 6/8 has a fine but permeable resin layer. The products can be readily dehydrated. In the case of example 6/10—13 the emulsions are mixed at 32° C and cured at 95° C. Variant C is used for the performance thereof. These examples show that the dispersion level setting also changes on changing the polymerisation conditions. In examples 6/10 and 6/12 samples are obtained which reveal a pronounced resin deposition on the surface whilst the inner portion of the samples consist of a coarse to fine porous cellular structure. In examples 6/11 and 6/13 the resin separation is considerably reduced. All hot-cured products have an elevated water loss during polymerisation and a decelerated drying at 23° C. In the case of samples 6/11 and 6/13 somewhat larger quantities of water can be removed by suction filtering. However, drying after 96 hours as compared with the cold cured products shows only a limited water loss, between 33 and 50%.

The examples show that the properties of the cured water-in-oil emulsions are dependent on the dispersion level to which they are set, and reveal considerable differences which have hitherto not been recognised or evaluated.

Whereas the absolutely stable water-in-oil emulsion, which even under the influence of curing does not vary its stability behaviour, reveals only slight variations in the cured products and is unsuitable for producing moulded articles with a stable material structure particularly those which rapidly give off water without auxiliary measures being taken, the setting of the dispersion level in the still unstable range permits the setting of optimum desired characteristics.

By means of the examples it is finally proved that the cured sample accompanied by airing at normal room temperature of 23° C can be dehydrated in extremely short times, and that the samples with an increase in water

content in the emulsion reveal a clear acceleration in drying. All samples reveal a distinct capillary activity i.e. they rapidly absorb liquids which are applied dropwise. Depending on whether the resin types is more or less hydrophobic or hydrophilic water or organic solvents are more rapidly absorbed.

In the following example a special form of processing of the emulsion according to the invention by spraying and moulding with fillers of glass and natural fibres is demonstrated.

A mixture of two emulsions is prepared according to example 4/10 changing the proportion of water to 125 parts by weight. Emulsion 1 contains the peroxide in double quantity, emulsion 2 the accelerator in double quantity. Both emulsions are set to a viscosity of 1000 cP by shortening the stirring time to 90 sec. In each case the formulation quantity is 10,000 g. For the preparation of the emulsion correspondingly larger stirring devices are used. Prior to use the two emulsions are mixed in the ratio 1:1 by weight.

In the first test 200 g of emulsion 1 and 200 g of emulsion 2 are used to produce moulded articles. Two glass fibre mats (600 g/cm^2) are placed in a 20 × 20 cm plate mould with a spacing of 0.4 cm. The mixed emulsion is placed on the glass fibre mat and the mould is closed with a pressure of 15kg/cm^2. After 15 minutes and removal from the mould a plate is obtained which is reinforced with glass fibres which after airing at 23° C for 24 hours has a density of 0.75 g/cc. The same test is performed with sisal fibres and the finished plate has a density of 0.65.

5 g of emulsion 1 and 5 g of emulsion 2 are used for spraying with glass fibres. Emulsions 1 and 2 are placed in the pressure vessel of a fibre spraying installation. The emulsion is sprayed with glass fibres onto a 0.5 cm thick PTFE foil placed vertically on a wall. As a result of the addition of glass fibres and spraying of the emulsion the viscosity of the mixture increases to such an extent that the sprayed layer does not run off. After curing and drying a glass fibre reinforced sheet is obtained with a density of 0.85 g/cc and a glass content of approximately 20% by weight.

3 kg of the emulsion are mixed and the mixture is poured vertically into a plate mould with internal dimensions 10 × 40 × 75 cm, filled with glass foam balls of average diameter 20 mm.

In order to keep the specifically lighter foam balls in position the material is fixed at its surface by wire netting to provide protection against lift. The cast emulsion fills all the voids and, after curing and mould removal after 20 minutes and after drying at 30° C accompanied by airing for 24 hours, a 10 cm well-filled sheet of high strength and a density of 0.5 g/cc is obtained.

These tests show that the emulsions according to the invention with fillers can also be completely satisfactorily processed by spraying and moulding and that also filled members give off the water in a very short time.

The tests performed in the glass fibre spraying process were repeated. 400 × 800 mm plates were produced in thicknesses between 3 and 15 mm. The glass fibre content based on the emulsion varied between 5 and 33% by weight; the glass fibre length in the different samples was set to 3, 12 and 25 mm. In addition to the plates produced by spraying from the same material but with an increase in the viscosity from 1000 to 1500 cP glass fibres were mixed in the emulsion and cast into plates as described hereinbefore. After curing the plates were dried and at 23° C there was a residual moisture content of 20% by weight after 48 hours in the case of the 15 mm thick plates and of only 15% by weight in the case of the 5mm thick plates. The plates are absolutely planar without any distortion. Samples were taken from the plates and tested for bending strength. The results are given in Fig. 6. It was shown that the bending strength given by small additions of glass fibres to the emulsion rose rapidly by several hundred percent. No difference was noted between the sprayed samples and those produced by mixing in glass fibres. However, it was found that the glass fibre length plays a not unimportant role and the bending strength with increasing length rapidly increases up to about 30 mm.

The test show that contrary to carrier experience in this connection whereby the addition of glass fibres led to pronounced distortion of emulsion foams, according to the new process moulded articles are obtained having a very high dimensional stability. It has been found that this occurs in particular if the glass fibres are uniformly distributed in small quantities in the product, whereby then considerable tolerances in the thickness have no influence on the dimensional stability.

In Tables 4 to 6 which follow the symbol "X" indicates that the figure is the same as that given for the immediately preceding Test Number.

Unsaturated polyester resins	1. Commercial product of maleic and phthalic anhydride and propylene glycol; styrene content 35%, viscosity 650 to 1000 cP at 20°C, acid number below 30 = UP 1
	2. WEP 12 (unsaturated polyester resin modified with styrene – manufacturer Ashland) = W 12
	3. WEP 26 (unsaturated polyester resin modified with styrene – manufacturer Ashland) = W 26
	4. Soft commercial cast resin, styrene content 30%, viscosity 950 to 1200 cP at 20°C, iodine colour value max. 2 = UP 2.
Polymers	1. Polymethyl methacrylate (suspension polymer of approx. 95% MMA and 5% butyl acrylate): particle size approx. 20 to 50μ = PM.
Monomers	1. Styrene = St
	2. Methyl methacrylate = MMA
	3. Acrylonitrile = AN
	4. Butyl acrylate = ASB
	5. Ethylene glycol dimethacrylate = EGM
Peroxides	1. 50% benzoyl peroxide = BP
	2. 50% methyl ethyl ketone peroxide = MEK
Accelerators	1. Dimethyl aniline = DM
	2. 50% dimethyl-p-toluidine = DMT
	3. 6% cobalt octoate = KOB
Inhibitor	1. C 10 (manufacturer Oxido)
Emulsifiers	1. Pluronic 105 = P 105
	2. Pluronic 123 (manufacturer Wyandott) = P 123
	3. Pluronic 108 = P 108
	4. Emu-powder (manufacturer BASF) = EP
	5. Pril (manufacturer Henkel) = Pr ("Pril" is a registered Trade Mark)
	6. Emulsifier A according to Belgian patent 785.091 = E.A (emulsifier from ethoxilated novolaks or phenols)
	7. Pluronic 122 = P 122

TABLE 4

Test number	1	2	3	4	5	6	7	8	9	10	11	12
Resins	UPI											
	80	x	x	x	x	x	x	x	x	x	x	x
Accelerators	DMT											
	0.3	x	x	x	x	x	x	x	x	x	x	x
Emulsifiers	EP 0.01	0.5	1.0	0.01	0.05	1.0	P122 0.5	x	1.0	P123 1.0	x	x
				Pr 0.05	x	x	P103 0.5	x	1.0			
H_2O	100	x	x	x	x	x	x	x	x	200	240	300
Stirring time in sec.	150	x	x	x	x	x	60	150	x	150	x	x
Emulsion temp. °C	21	23	x	x	x	x	25	x	x	24	x	x
Viscosity cP	300	600	700	350	400	650	580	650	1600	2500	3000	3500
Gelling time in min.	7	6	x	x	x	x	11	x	x	14	12	10
Weight after removal from mould in g	164	164	169	164	164	169	163	161	164	167	168	167
Weight after suction filtering in g	148	163	168	145	140	160	118	111	124	100	96	83
Weight loss as a percent of total weight	25.8	8.2	2.4	29.4	35.3	11.8	61.2	69.4	54.1	59.8	62.2	68.2

TABLE 4 (Continued)

Test number	1	2	3	4	5	6	7	8	9	10	11	12
a) Weight loss after 24 h as % of total wt.	37.6	18.8	7.0	45.8	53.0	11.8	76.4	94.1	90.5	98.2	94.1	98.1
b) Weight loss after 24 h as % of total wt.										89.2	[illegible]	90.2
c) Weight loss after 96 h as % of total wt.	64.7	41.1	11.2	64.7	76.4	11.8	96.0	98.2	98.1	100	99.0	100

The weight loss is detemined 24 hours after removal from the mould of

a) a sample partially dehydrated by suction filtering.

b) a sample which has not been suction filtered,

c) weight loss 96 hours after removal from the mould

In each case, the weight loss was determined from a sample with a ratio of surface to volume of 1.17 which was dried at a temperature of 23°C and a relative humidity of 60%.

TABLE 5

Test number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Resins	W 12	W 26	W 12									W 12 W 26		
	100	x	x	x	x	x	x	x	x	x	x	1:1 by wt. 100	x	x
Peroxides	MEK 2.0	x	x	x	x	x	x	x	x	x	x	x	x	x
Accelerators	Kob 3.3	x	x	x	x	x	x	x	x	x	x	x	x	x
	DM 0.25	x	x	x	x	x	x	x	x	x	x	x	x	x
Inhibitors	C10 0.1	x	x	x	x	x	x	x	x	x	x	x	x	x
Emulsifiers			P108			P105			P123			E.A		
			0.5	1.0	2.0	0.025	0.5	1.0	0.5	1.0	2.0	1.0	2.0	3.0
H_2O	100	x	x	x	x	x	x	x	x	x	x	x	x	x
Stirring time in sec.	150	x	x	x	x	x	x	x	x	x	x	x	x	x
Emulsion temp. °C	20	x	x	x	x	x	x	x	x	x	x	x	x	x
Viscosity cP	700	900	650	650	950	1300	1500	1600	2200	2300	2500	2100	2900	3000
Gelling time in min.	9	8	8.5	6.5	5.5	10	8.5	7.5	5.5	6	5	9	7	6

TABLE 5 (Continued)

Test number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Weight after removal from mould in g	168	169	168	169	168	168	168	168	165	168	168	160	162	163
Weight after suction filtering in g	168	168	166	169	168	155	166	167	150	164	164	157	148	145
Weight loss as a percent of total wt.	2.4	2.4	4.7	1.1	2.4	17.5	4.7	3.5	23.5	7.0	7.0	15.3	25.8	29.4
a) Weight loss after 24 h as % of total wt.	2.4	2.4	4.7	3.5	3.5	45.8	9.4	4.7	54.1	35.3	25.8	68.2	61.2	54.1
b) Weight loss after 24 h as % of total wt.														
c) Weight loss after 96 h as % of total wt.	2.4	2.4	5.8	4.7	8.2	84.7	14.1	11.7	88.2	68.2	64.7	88.2	80.0	77.6

The weight loss is determined 24 hours after removal from the moulds of

a) a sample partially dehydrated by suction filtering,

b) a sample which has not been suction filtered,

c) weight loss 96 hours after removal from the mould

In each case, the weight loss was determined from a sample with a ratio of surface to volume of 1.17 which was dried at a temperature of 23°C and a relative humidity of 60%.

TABLE 6

Test number	1	2	3	4	5	6	7	8	9	10	11	12	13
Resins	W12 50 W12 50	x	x	UP 1 40	x	x	x	UP 2 67.5	x	UP 1 80	x	x	x
	W26 50	x	x	UP 2 40	x	x	x						
Polymer								PM5	x				
Monomers				MMA				AN 10 ASB 15	x	St		MMA	
				20	x	x	x	EGM 2.5	x	20	x	20	x
Peroxides	MEK 2.0	x	x	BP 3.0	x	x	x	x	x	2.0	x	x	x
Accelerators				DMT						DMA			
				0.3	x	x	x	x	x	0.3	x	0.2	x
Inhibitors	C10 0.1	x	x	–	–	–	–	–	–	–	–	–	–
Emulsifiers	P105			P127 P105	E.A			P104		P105			
	0.05	0.1	0.2	0.25 0.25	1.0	2.0	3.0	1.0	2.0	1.0	1.5	0.2	0.5
H_2O	100	x	x	x	x	x	x	x	x	x	x	x	x
Stirring time in sec.	150	x	x	90	150	x	x	x	x	x	x	x	x

TABLE 6 (Continued)

Test number	1	2	3	4	5	6	7	8	9	10	11	12	13
Emulsion temp. °C	22	x	x	25	20	x	x	25	x	32 95	x	x	x
Viscosity cP	2300	3700	4700	2400	1500	2200	2700	1200	1800	700	1300	2500	3000
Gelling time in min.	6	4	5	8	10	7	6	8	7	4.5	4	6	x
Weight after removal from mould in g	159	158	160	165	164	166	167	165	168	157	162	158	161
Weight after suction filtering in g	156	148	147	114	113	114	117	125	130	156	145	158	153
Weight loss as a percent of total wt.	16.4	25.8	27.0	65.8	67	65.8	62.3	52.9	47.0	16.4	29.4	14	20
a) Weight loss after 24 h % of total wt.	70.5	76.4	82.3	91.76	88	82.3	72.9	71.0	65.0	20	47	28.2	36.4
b) Weight loss after 24 h % of total wt.					58.8	64.7	64.7	65.0	58.0	20	35.8	37.7	25.8
c) Weight loss after 96 h % of total wt.	88	88	94	98.5	89	76	76	90	85	33	50	33	45

The weight loss is determined 24 hours after removal from the mould of

a) a sample partially dehydrated by suction filtering,

b) a sample which has not been suction filtered.

c) weight loss 96 hours after removal from the mould.

In each case, the weight loss was determined from a sample with a ratio of surface to volume of 1.17 which was dried at a temperature of 23°C and a relative humidity of 60%.

WHAT I CLAIM IS:—

1. A process for producing shaped articles with a cellular structure which comprises shaping and curing an emulsion comprising from 25 to 90 parts by weight of water dispersed in from 75 to 10 parts by weight of a liquid synthetic resin-monomer mixture comprising styrene and/or a methacrylic or acrylic acid ester and a copolymerisable unsaturated polyester or copolymer of styrene and butadiene, the emulsion having a dispersion level which is in the characteristic range (as herein defined) prior to commencement of curing and the curing being effected at a rate whereby the emulsion gels before commencement of disintegration of the emulsion.

2. A process as claimed in claim 1 wherein one or more further ingredients selected from curing catalysts, emulsifying agents, wetting agents, accelerators, inhibitors, cross-linking compounds, softeners, fillers and dyes are added to the emulsion prior to curing.

3. A process as claimed in either of the preceding claims wherein the dispersion level of the emulsion is adjusted prior to commencement of curing by the addition of an emulsifying agent.

4. A process as claimed in any of the preceding claims wherein the synthetic resin-monomer mixture comprises an unsaturated polyester dissolved in a mixture of styrene and methyl methacrylate in a weight ratio of from 1:4 to 4:1.

5. A process as claimed in any of the preceding claims wherein the emulsion contains an emulsifying agent comprising one or more organic compounds containing from 28 to 55% by weight of ($-CH_2-CH_2-O-$) groups as a hydrophilic component and a base with a molecular weight of at least 2000 as a hydrophobic component.

6. A process as claimed in any preceding claims wherein the emulsion is shaped to form the desired article in a mould.

7. A process as claimed in claim 6 wherein the water-in-oil emulsion is poured into the mould in layers of varying dispersion level.

8. A process as claimed in any of the preceding claims wherein the water-in-oil emulsion is mixed with a filler prior to curing.

9. A process as claimed in claim 8 wherein the filler comprises glass fibres.

10. A process as claimed in any of the preceding claims wherein the cured emulsion is subsequently dried.

11. A process as claimed in claim 10 wherein the cured emulsion is dried under vacuum.

12. A process as claimed in claim 10 wherein the cured emulsion is dried in a drier with air circulation.

13. A process as claimed in any of the preceding claims substantially as herein described.

14. Shaped articles with a cellular structure when produced by a process as claimed in any of the preceding claims.

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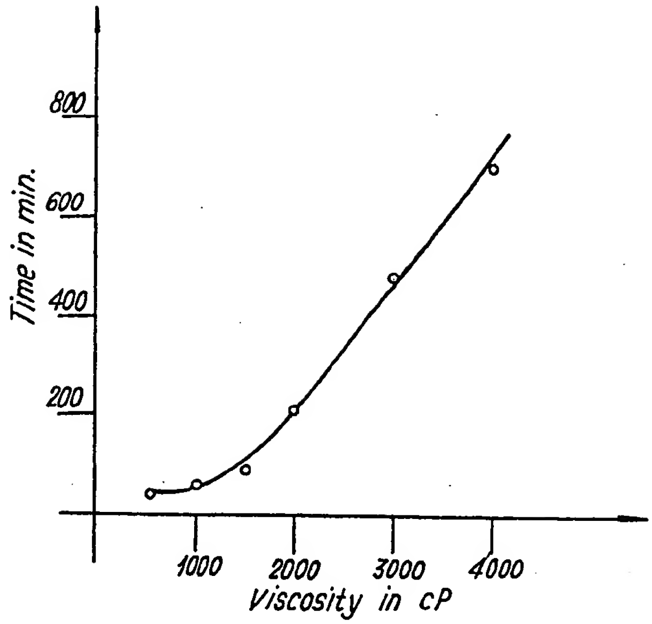

Time in min.
800
600
400
200
1000
2000
3000
4000
Viscosity in cP

Fig.1.

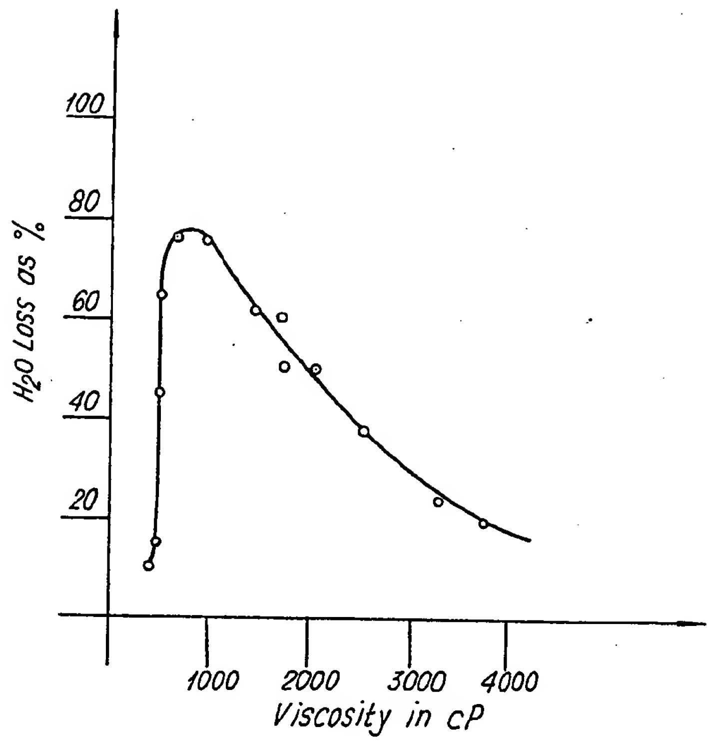


Fig.2.

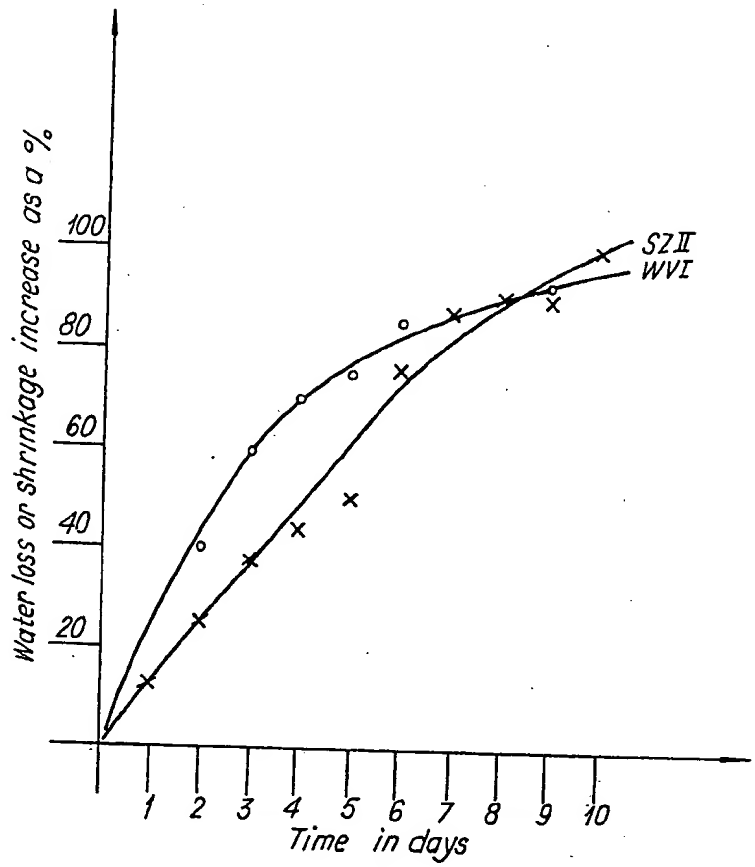
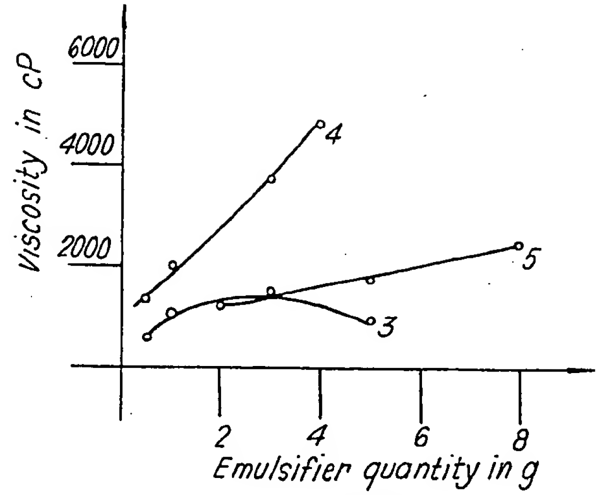

Water loss or shrinkage increase as a %
100
80
60
40
20
1
2
3
4
5
6
7
8
9
10
Time in days
SZII
WVI

Fig.3.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4000
2000
4
5
3
2
4
6
8
Emulsifier quantity in g

Fig.4.

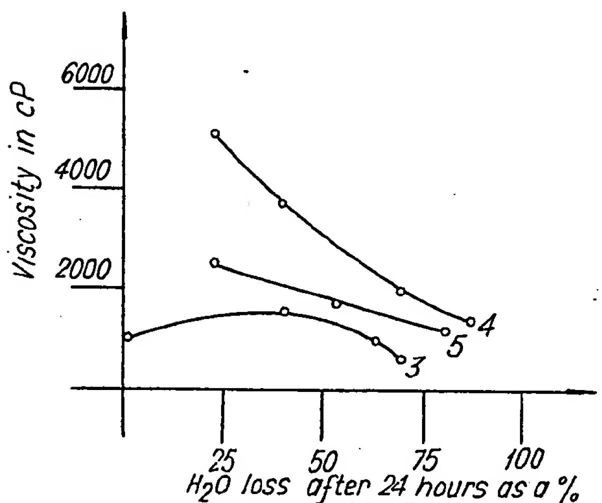
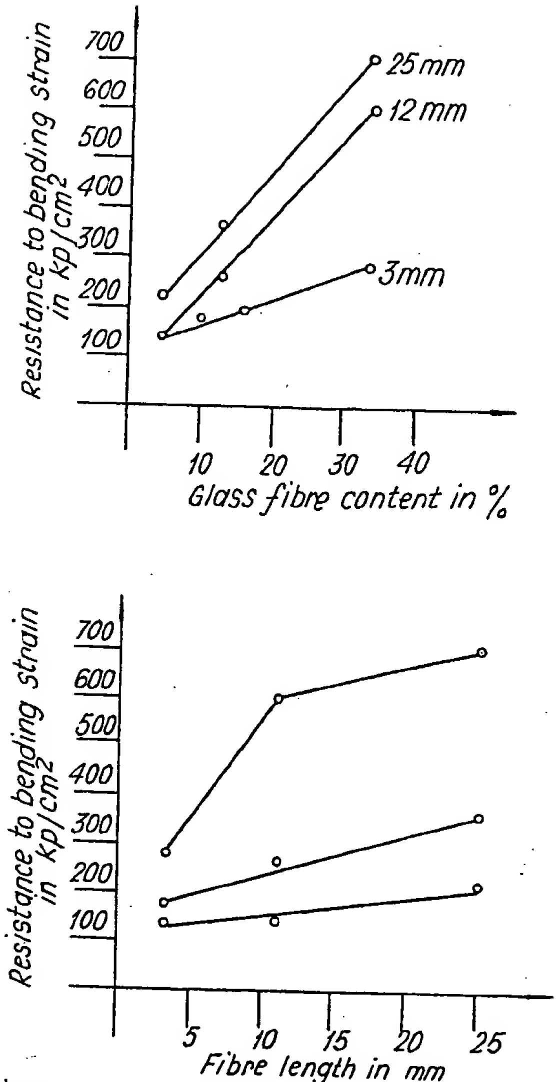

Viscosity in cP
6000
4000
2000
4
5
3
25
50
75
100
H2O loss after 24 hours as a %

Fig.5.



Resistance to bending strain of an emulsion (water content 45%) in relation to the glass fibre content and glass fibre length.

Fig.6.